A New Phase of the c(4 × 2) Superstructure of Alkanethiols Grown by Vapor Phase Deposition on Gold

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A self-assembled monolayer of dodecanethiol is grown onto (111) oriented gold by vacuum phase deposition and studied by ultrahigh vacuum scanning tunneling microscopy (STM). The films consist of domains that exhibit the c(4 × 2) overstructure of the hexagonal ($\sqrt{3} \times \sqrt{3}$)R30 of alkanethiols on gold. The domain size is only limited by the terrace size of the underlying gold. By higher resolution scans a new phase of the c(4 × 2) structure consisting of four inequivalent molecules that display different heights in the STM images is discovered.

As a result of their potential applications, for example, in molecular electronics,[1,2] corrosion protection,[3] and lateral structuring,[4] and their high structural order,[5] self-assembled monolayers (SAMs) of organic materials have been intensively studied in recent years. The most thoroughly studied systems are SAMs of alkanethiols on gold.[6]

These SAMs are known to form a ($\sqrt{3} \times \sqrt{3}$)R30 overlayer on the (111) surface of gold, which is further structured by a c(4 × 2) or ($2\sqrt{3} \times 3$) superstructure.[7−10] The superstructure is characterized by systematic arrangement of molecules showing a distinct height difference in STM images.

This height difference in STM images is believed to be due to different conformations of the molecule. Because the molecular backbone is tilted ∼30° out of the surface normal, the terminal methyl group appears higher or lower, if the molecule is twisted. For a full rotation, a maximal height difference of 0.6−0.7 Å is expected.[7,9] Similary, different bonding sites of the sulfur headgroup on the gold surface, as observed by grazing incidence X-ray diffraction,[11] sum frequency generation,[12] and X-ray standing wave[13] and high-resolution electron-energy-loss spectroscopy,[14] lead to different heights in scanning tunneling microscopy (STM) images. Additionally, by different bonding sites the tunneling conditions vary, which adds further contrast in STM images. For example, Fenter et al.[11] propose that the sulfur headgroup dimerizes, resulting in a S−S spacing of ∼2 Å and two inequivalent bonding sites (threefold hollow site and Au bridge site). He argues that the height modulation in STM images is due to the inequivalent bonding site, resulting in different tunneling conditions and different twists of the hydrocarbon chains about the chain axis.

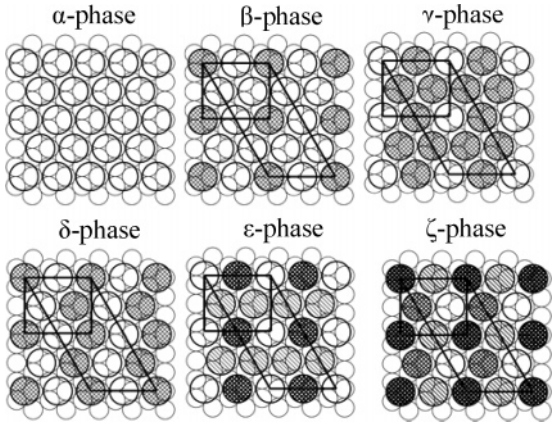

Figure 1. ($\sqrt{3} \times \sqrt{3}$) structure (α phase) and different phases of c(4 × 2) of C12 SAMs. Higher molecules are shaded dark. The phase observed here is denoted as the ζ phase.

Different arrangements of apparently higher and lower molecules are described in the literature[8,9,15−17] denoted as phase α to ϵ (see Figure 1). The α phase is the normal ($\sqrt{3} \times \sqrt{3}$) structure without any superlattice, the β,[9,15] γ,[15] and δ[8,9,15,17] phases consist of molecules with two different heights. More recently, a c(4 × 2) structure with three different molecular heights was discovered in octanethiol (C8) and dodecanethiol (C12) SAMs (ϵ phase).[16,17]

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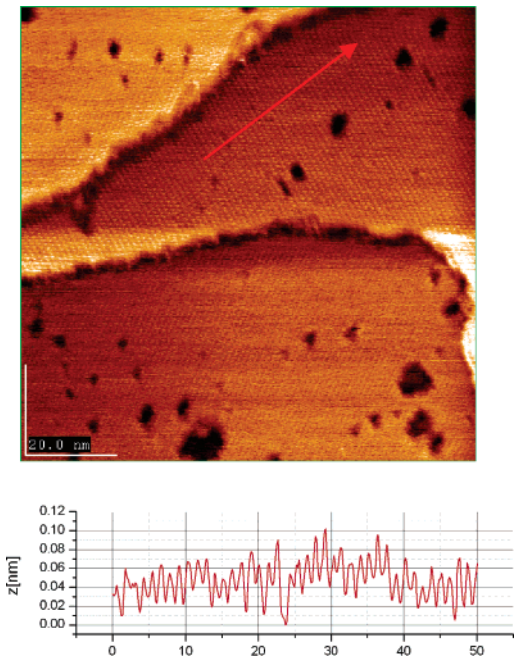

Figure 2. 100 × 100 nm² STM image of the C12 SAM. V_t = 1.59 V, I_t = 50 pA.

The easiest way to grow a SAM of alkanethiols is to immerse a gold film into a solution of the molecules. However, for clean and highly ordered surfaces growth from the gas phase is superior.[18−20] In this study, we present SAM films grown from the gas phase, which show domains, that are only limited by the size of the terraces of the underlying gold film and which show a new c(4 × 2) phase with four different heights.

The SAMs presented here are grown onto (111) oriented gold and deposited onto mica in a two-step process, which results in large terraces and low surface roughness.[21] The C12 SAM is deposited onto the gold film in a special designed vacuum chamber. A glass tube filled with C12 is attached to the vacuum chamber. The stream of C12 molecules is directed via a valve and a nozzle to the gold film. The exposure of molecules is measured by the pressure increase in the vacuum chamber (2×10^{-5}) times the deposition time (30 min). In units of langmuir, this corresponds to an exposure of 27 000 langmuir, which is high enough to ensure that a dense monolayer of the c(4 × 2) phase is built.[19] Following deposition, the film is transferred to an ultrahigh vacuum scanning tunneling microscope (JEOL JSPM 4500, base pressure 3×10^{-10} mbar).

A large area scan of the film is shown in Figure 2. Several gold terraces are visible. The monolayer of C12 is seen by a stripe pattern with a periodicity of 1 nm, which indicates the c(4 × 2) structure, without up to now revealing the exact phase of the c(4 × 2) structure. Remarkable is the size of the domains of C12. No domain boundaries can be seen, and the domains extend over the whole gold terrace.

Compared to other STM images of SAMs of alkanethiols, the one gold atom deep vacancy islands are not connected by domain boundaries and there is a large variation in size of the vacancy islands.

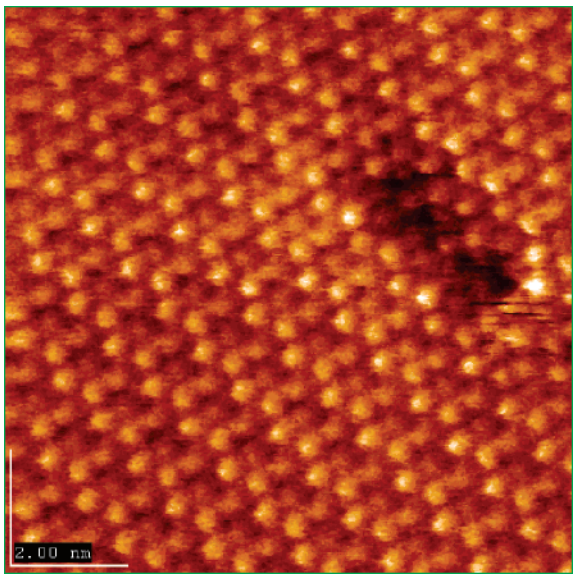

Figure 3. δ phase of the c(4 × 2) structure of the C12 SAM. The film is grown at an exposure of 27 000 langmuir. V_t = 1.59 V, I_t = 50 pA; image size, 9.7 × 9.7 nm².

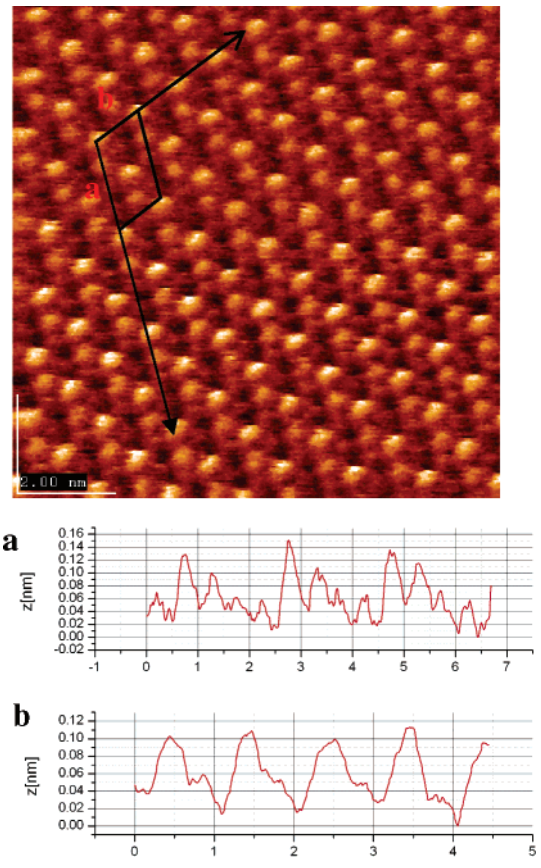

Figure 4. New c(4 × 2) structure with four inequivalent molecules. The film is grown at an exposure of 27 000 langmuir. V_t = 1.55 V, I_t = 45 pA. Image size: 10 × 10 nm².

Such large domains of alkanethiol SAMs can be grown from solution only by an additional annealing step.[22] Since Kondoh et al.[19] also showed large area domains of a hexanethiol (C6) SAM grown by vapor deposition, this effect seems to be due to different growth dynamics of vapor phase growth compared to growth from solution.

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In high-resolution images, the c(4 × 2) reconstruction can be resolved (Figures 3 and 4). Two different phases of c(4 × 2) can be identified: the normal δ-phase with two different heights in each unit cell (Figure 3) and a new phase with four different heights (Figure 4). The height differences are shown in the cross sections a and b. Along cross section a, there are groups of four molecules, in which each molecule appears approximately 0.3 Å lower than the preceding molecule. Along cross section b, one high molecule and one low molecule alternate. This pattern leads to the ζ phase shown in Figure 1. Because we are able to resolve both phases, the normal δ phase and the new ζ phase, on the same sample with the same tip and the same scanning parameters, we can exclude that the new phase is due to tip artifacts.

The new ζ phase can be explained based on the disulfide model of Fenter et al.,[11] the twisting of the molecules, or a combination of both. A slight modification of the disulfide model, which results in its original form in two different STM heights, can account for the here presented height modulation. More than two inequivalent bonding sites of the sulfur headgroup on the Au(111) surface or likewise two different bonding sites of the disulfides on the gold substrate would lead to different tunneling conditions and to four molecules having different heights in STM images.

Similarly, if one assumes more than two twist angles in the unit cell, one could also explain the structure presented here. The maximum height difference observed in our structure (∼0.9 Å) is close to the maximum height difference that can be explained by a twist of the molecular backbone.[9] Because STM cannot distinguish between real height differences due to a twist of the molecules and differences in tunneling conditions due to inequivalent bonding sites, the structure shown in Figure 4 can be explained by both theories.

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